Fig. 3. Mass from blood of young rat (in serum) in full development, after two hours' warming. (Ocular 3, Objective 7.)
Fig. 4. Mass (young rat) with blood-corpuscles about it, to show the relative sizes. (Ocular 3, Objective 5.)
Fig. 5. Some of the developed forms as seen with No. 11 Hartnack. (See text.)
Fig. 6. Form watched for four hours. (Ocular 3, Objective 9.)
Fig. 7. Form watched for five hours. (Ocular 3, Objective 9.)
Fig. 8. Small vein in connective tissue from the back of a young rat, showing the corpuscles free among the red ones. (Ocular 3, Objective 7.)
Fig. 9. Small vein from the connective tissue of a rat (in serum), showing corpuscles and developed forms. (Ocular 3, Objective 9.)

VII. "On Coniferine, and its Conversion into the Aromatic Principle of Vanilla." By Ferd. Tiemann and Wilh. Haarmann. Communicated by A. W. Hofmann, LL.D., F.R.S. Received May 11, 1874.

The sap of the cambium of coniferous trees contains a beautiful crystalline glucoside, coniferine, which was discovered by Hartig and examined some years ago by Kubel, who arrived at the formula

$$C_{24}H_{32}O_{12} + 3aq.$$

A minute study of this compound leads us to represent the molecule of coniferine by the expression

$$C_{16}H_{22}O_8 + 2aq,$$

the percentages of which nearly coincide with the theoretical values of Kubel's formula.

Submitted to fermentation with emulsine, coniferine splits into sugar and a splendid compound, crystallizing in prisms which fuse at 73°. This body is easily soluble in ether, less so in alcohol, almost insoluble in water; its composition is represented by the formula

$$C_{10}H_{12}O_3.$$

The change is represented by the equation

$$C_{16}H_{22}O_8 + H_2O = C_6H_{12}O_6 + C_{10}H_{12}O_3.$$

Under the influence of oxidizing agents the product of fermentation undergoes a remarkable metamorphosis. On boiling it with a mixture of potassium bichromate and sulphuric acid, there passes with the vapour of water, in the first place ethylic aldehyde, and subsequently an acid compound soluble in water, from which it may be removed by ether. On evaporating the ethereal solution, crystals in stellar groups are left behind, which fuse at 81°. These crystals have the taste and odour of vanilla. An accurate comparative examination has proved them to be iden-

tical with the crystalline substance which constitutes the aroma of vanilla, and which is often seen covering the surface of vanilla-rods.

On analysis, the crystals we obtained were found to contain

$$C_8 H_8 O_3.$$

This is exactly the composition which recent researches of Carles have established for the aromatic principle of vanilla. The transformation of the crystalline product of fermentation into vanilline is represented by the following equation :—

$$C_{10} H_{12} O_3 + O = C_2 H_4 O + C_8 H_8 O_3.$$

To remove all doubt regarding the identity of artificial vanilline with the natural compound, we have transformed the former into a series of salts which have the general formula

$$C_8 H_7 MO_3,$$

and into two substitution-products,

$$C_8 H_7 Br O_3$$

and

$$C_8 H_7 I O_3,$$

both of which had previously been prepared by Carles from the natural compound.

In order further to elucidate the nature of vanilline, we have submitted this body to fusion with alkali. The product of this action is a well-known acid discovered by Strecker, and described by him as proto-catechuic acid,

$$C_7 H_6 O_4,$$

which is thus formed—

$$C_8 H_8 O_3 + 4 O = C_7 H_6 O_4 + H_2 O + CO_2.$$

We have identified this substance by analysis, by the study of its reactions, and also by transforming it into pyrocatechine, $C_6 H_6 O_2$,

$$C_7 H_6 O_4 = C_6 H_6 O_2 + CO_2.$$

The transformation into protocatechuic acid fixes the constitution of vanilline. This compound is the methylated aldehyde of protocatechuic acid; its composition referred to benzol is represented by the formula

$$C_6 H_3 \begin{cases} O\,C\,H_3 \\ O\,H \\ C\,O\,H. \end{cases}$$

Indeed, submitted under pressure to the action of hydrochloric acid, vanilline splits into chloride of methyl and protocatechuic aldehyde,

$$C_6H_3\begin{cases}OCH_3\\OH\\COH\end{cases} + HCl = CH_3Cl + C_6H_3\begin{cases}OH\\OH\\COH.\end{cases}$$

A corresponding action takes place with hydriodic acid; but in this case the aldehyde is destroyed.

An additional proof of the correctness of our view regarding the constitution of vanilline is obtained by treating this substance with acetic anhydride and benzoyl chloride.

The action does not go beyond the formation of the compounds

$$C_6H_3\begin{cases}OCH_3\\OC_2H_3O\\COH,\end{cases}$$

and

$$C_6H_3\begin{cases}OCH_3\\OC_7H_5O\\COH,\end{cases}$$

showing that vanilline does not contain more than one hydroxylic group.

The constitution of vanilline being thus made out, there could be no doubt regarding the structure of the product of fermentation from which vanilline arises. This compound is the ethylic ether of vanilline,

$$C_6H_3\begin{cases}OCH_3\\OC_2H_5\\COH.\end{cases}$$

That such is the constitution of the body is proved by the simultaneous formation of ethylic aldehyde when vanilline is formed. We obtained, however, an additional confirmation of this conception by submitting the product of fermentation to the action of hydriodic acid under pressure, when an alcohol iodide was formed, which we succeeded in separating into the iodides of methyl and ethyl,

$$C_6H_3\begin{cases}OCH_3\\OC_2H_5\\COH\end{cases} + 2HI = CH_3I + C_2H_5I + C_6H_3\begin{cases}OH\\OH\\COH.\end{cases}$$

The experiments we have described in this note were performed in the laboratory of Professor A. W. Hofmann, to whom we are deeply indebted for the advice and assistance he has given us in the course of these researches.